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Mixed Alkali Effect on Calcium Aluminogermanate Glasses

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Abstract: Germanate glasses containing 0–6.44 wt% Li_2O were prepared by progressive weight percent substitution of Na_2O for Li_2O, at a constant ratio of concentration of CaO, Al_2O_3 and GeO_2. The mixed alkali effect on the optical properties, chemical resistance and electrical resistivity of calcium aluminogermanate glasses have been studied. The results of FT–IR spectra show that absorption band in 800–900 cm^{-1} region corresponds to GeO_4 groups and the Ge remains in 4-coordination state for these germanate glasses. As $0 \leq Na_2O/(Li_2O+Na_2O) \leq 0.5$, the refraction index of and reflectance decrease with increasing Na_2O content, during $1 \geq Na_2O/(Li_2O+Na_2O) \geq 0.5$, then its values are increasing with increasing Na_2O content. The leaching results indicate that $Haze_{uv}$ values for these germanate glasses with different content of Li_2O and Na_2O are greater than those of glasses containing only Li_2O or Na_2O, but the variations of pH value when the glasses are immersed in acidic solutions are greater in single alkali germanate glasses than in mixed alkali glasses. For the electrical resistivity measured, a maximum value occurs at $Na_2O/(Li_2O+Na_2O) = 0.5$. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

It is not surprising that good glasses can be formed with GeO_2 as the network former, as the outer electronic structure of germanium is the same as that for silicon. However, its larger atomic size implies a weaker bonding, yielding a better infrared transmission and a smaller range of stable glass formation than for silicates.[1] Although there have been a large number of studies concerning the properties and structure of $R_2O–Al_2O_3–GeO_2$ (or $R_2O–Al_2O_3–SiO_2–GeO_2$) glasses,[2–6] and the corresponding $MO–Al_2O_3–GeO_2$,[1,7] an extensive literature search showed that details of the chemical resistance, electrical resistivity and structure related to mixed alkali calcium aluminogermanate glass system have not been elaborated.

The pronounced changes in properties resulting from the addition of a second alkali oxide to a glass has been called the mixed alkali effect.[8] The most prominent mixed alkali effect for oxide glasses is the pronounced reduction in DC conductivity observed for systems with two or more different types of alkali components.[8,9] A knowledge of the change in properties with chemical composition is important to the glass technologist. Since the glass composition must be capable of being melted and shaped by economical methods, the influence of composition must be considered in formulating glasses for infrared materials. In germanate glass, the composition, raw materials selection and substitution are extremely important.

In the present article, the chemical resistance, electrical resistivity and structure of mixed alkali calcium aluminogermanate glasses were studied. The purposes of this investigation are: (i) to evaluate the impact of the mixed alkali effect on the chemical durability; (ii) to confirm the influence of the mixed alkali effect on the electrical resistivity;

and (iii) to determine the mixed alkali effect on the structure of these glasses.

2 EXPERIMENTAL

The starting materials used for preparing the glasses were electronic grade GeO_2 and the analytical grades of: Li_2CO_3, Na_2CO_3, Al_2O_3 and $CaCO_3$. Glass compositions are listed in Table 1. Na_2O was introduced in 1.61 wt% stepwise substitutions for the Li_2O. All samples were obtained in 10–20 g batches by melting in a platinum crucible at 1420 °C in an electric furnace for 2 h. After homogenizing, the melt was quenched in water, dried, and the crushed powder was remelted at 1420 °C for another 2 h, cast on to a hot stainless steel plate kept at 400 °C and transferred to an annealing furnace at 500 °C held for 1 h. Finally, clear, transparent and colourless glasses were obtained.

The glass samples for optical absorption measurement were about 2.0 mm thick, and were polished for parallel faces. The infrared spectra were recorded with a Hitachi Infrared Spectrometer Model 290-30. The absorption spectrum for ultraviolet was obtained with a Hitachi Ultraviolet Spectrophotometer model U-3210. The refractive index of these glass samples, which were polished for adjacent perpendicular faces, was measured as a function of Na_2O content in the infrared region with a V-prism refractometer. The chemical resistance of these glass samples was judged from its dissolution rate in distilled water with initial pH = 6.33 at 30 °C for 70 h and 103 h. The leached samples were dried at 105 °C for 2 h. The transmittance in the 500–800 nm region was measured and calculated for the relative transmittance value ($\mathrm{Haze}_{\mathrm{uv}}$):

$$\mathrm{Haze}_{\mathrm{uv}} = \frac{T_{\mathrm{cor-vis}}}{T_{\mathrm{vis}}}$$

where:

(a) T_{vis}: the average transmittance in 500–800 nm before leaching.

(b) $T_{\mathrm{cor-vis}}$: the average transmittance in 500–800 nm after leaching.

The samples were leached in nitric acid solution with initial pH = 2.02 at 30 °C for various leaching time. After leaching, the samples were dried at 105 °C for 2 h. The pH value variation was measured from the corrosion after leaching in the acidic solution.

The samples for electrical resistivity measurement were about 11.0×6.0×6.0 mm. After grinding and polishing for parallel faces, the samples were daubed with silver gels and dried at 105 °C for 24 h. The electrical resistivity was recorded with a Hewlett-Packard 4329A High Resistance Meter.

Fourier transform infrared spectra (FT–IR) were measured in the 400–2000 cm^{-1} region using a Nicolet 800 system, with a resolution of 2 cm^{-1}; KBr pelletized disks were fabricated containing 2 mg of the glass sample and 600 mg KBr.

3 RESULTS AND DISCUSSION

The effect of mixed alkali on the ultraviolet transmittance cut-on for the calcium aluminogermanate glasses is shown in Fig. 1. Ultraviolet absorption edge for these glasses is near 306 nm, except for a glass containing Na_2O 6.44 wt% (C_5 glass) which lay at 295 nm. The ultraviolet absorption is caused by the excitation of the oxygens. Alkali germanate glasses accompany the presence of non-bridging oxygen.[2,5] In this study, according to FT–IR result, the higher the Li_2O content, the more non-bridging oxygens are present. For non-bridging oxygens the excitation energy is lower than that of bridging oxygens, consequently the absorption shifts to a

Table 1. Chemical composition of glasses (wt%)

Samples	Oxides				
	Na_2O	Li_2O	CaO	Al_2O_3	GeO_2
C_1	0	6.44	12.97	21.51	59.18
C_2	1.61	4.83	12.97	21.51	59.18
C_3	3.22	3.22	12.97	21.51	59.18
C_4	4.83	1.61	12.97	21.51	59.18
C_5	6.44	0	12.97	21.51	59.18

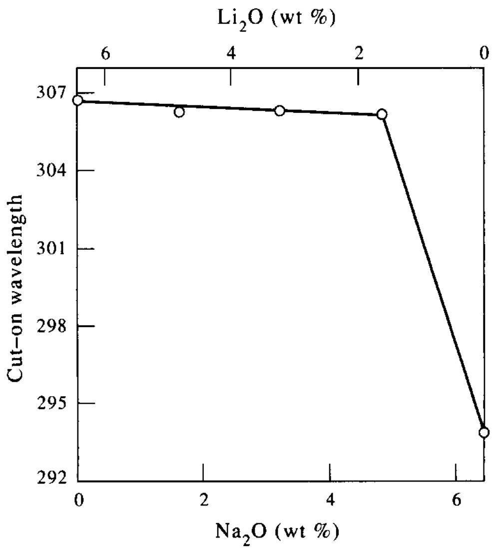

Fig. 1. The effect of mixed alkali on the ultraviolet transmittance cut-on for the calcium aluminogermanate glass.

longer wavelength with a weakening of oxygen bonding.[11]

FT–IR spectra of these germanate glass samples have two regions of absorption as shown in Fig. 2. The most intense absorption bands of these germanate glasses lie in the 800–900 cm^{-1} region, which may be assigned to antisymmetric stretching motions of GeO_4 tetrahedra containing bridging (i.e. Ge–O–Ge bond) and non-bridging (i. e. Ge–O$^-$ bonding) oxygens.[12–14] The second strong region of absorption lies between 500 and 600 cm^{-1} and may be related to mixed stretching–bending motions.[12] It can be assumed that in germanate glass the O–Ge–O (O–Ge–O$^-$) bending vibrations and symmetric stretching motions across the Ge–O–Ge bridging oxygens are coupled because of the small difference in frequency of these vibrations.[12] The coupling between these two modes produces the single broad band which is observed with an apparent frequency weighed according to the bend–stretch vibration frequencies and corresponding intensities.[12–14] This result shows that the peaks (800–900 cm^{-1}) in these glasses correspond to GeO_4 groups and the Ge remain in 4-coordination with mixed Li_2O and Na_2O.[7]

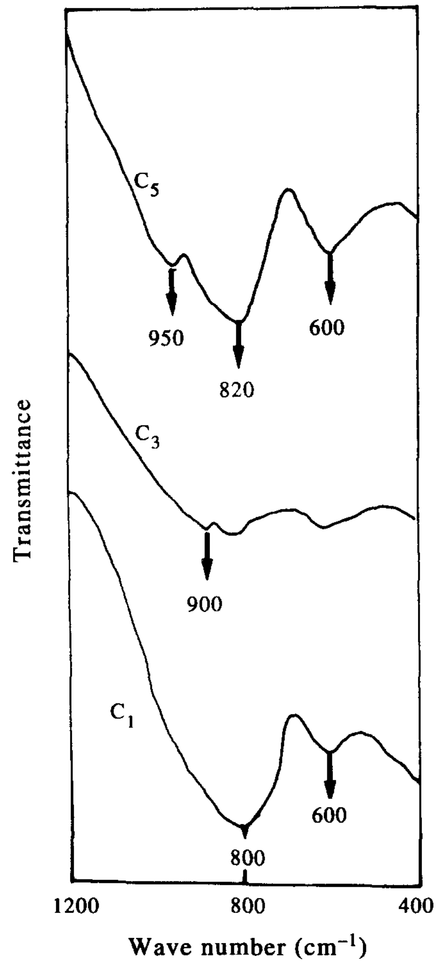

Fig. 2. FT–IR spectra for alkali calcium aluminogermanate glasses.

Refractive index controls reflection losses at interfaces between glasses and other materials. Figure 3 shows the effect of mixed alkali on the refractive index and reflectance of these calcium aluminogermanate glasses at 2.5 μm. The index of refraction increases along with the polarizability, although the immediate surroundings and arrangement of ions also affect the refractive index, but the outer electrons are less firmly bound in a negative ion than in a positive one; thus, in addition to the size effect, the outer electrons are expected to contribute the major share of the bulk polarizability.[15] Figure 3 shows that as $0 \leq Na_2O/(Li_2O + Na_2O) \leq 0.5$, the values of refractive index and reflectance decrease as the Na_2O content increases but when $1 \geq Na_2O/(Li_2O + Na_2O) \geq 0.5$, these values increase as the Na_2O content increases,

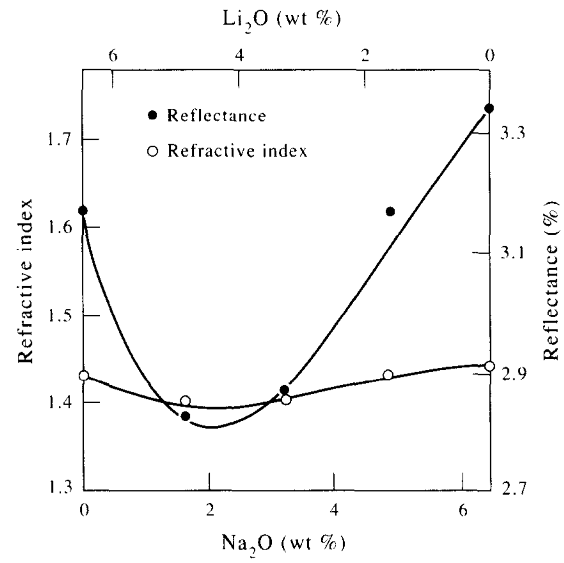

Fig. 3. Effect of mixed alkali on the refractive index and reflectance of calcium aluminogermanate glasses at 2.5 μm.

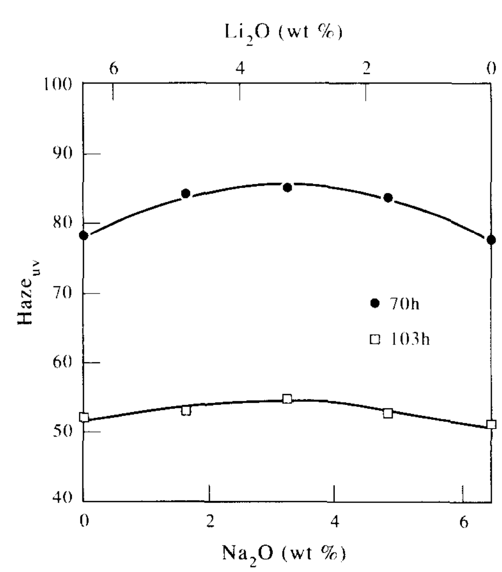

Fig. 4. Effect of mixed alkali content and leaching time at 30 °C on the Haze$_{uv}$ of calcium aluminogermanate glasses.

perhaps the size effect overcomes the change that occurs in polarizability.

The reaction of water with an alkali calcium aluminogermanate glass may be suggested to be initially controlled by diffusion and then by a surface reaction. Alkali calcium aluminogermanate glasses react with distilled water to form a hydrated germania-rich layer. Hydration proceeds by ion exchange between hydrogen ions from water and alkali ions in glass, with the formation of a gel-like hydrated layer on the glass surface.[16] In this gel-like layer, ions are quite mobile,[17] and water can penetrate to the gel–glass interface. During the later stage of reaction, the thickness of the gel-like hydrated layer becomes constant, the balance is determined by between the diffusion of ions through the gel layer, which thickens it, and the rate of removal of germanium at the gel layer–solution interface, which has the opposite effect.[18]

The effect of mixed alkali on the Haze$_{uv}$ of calcium aluminogermanate glasses is shown for different leaching times at 30 °C in Fig. 4. The Haze$_{uv}$ values of these germanate glasses with both Li_2O and Na_2O are greater than those of glasses containing only Li_2O or Na_2O (C_1 or C_5 glass). This may indicate that the mixed alkali affects the rate of gel layer–glass interface movement relative to the original glass interface; the rate of C_1 and C_5 glass is faster than that of C_2, C_3 and C_4 glasses. The thick gel layers formed on the less durable glasses are translucent in appearance and form a white friable crust when specimens are dried. The incident light is not only affected by film layer reflection and absorption, but is further affected by scattering caused by the friable crust, which decreases the transmittance.

The pH change of these mixed alkali calcium aluminogermanate glasses in nitric acid solution at an initial pH = 2.02 and 30 °C for various leaching time are shown in Fig. 5. The pH increase would be expected to suppress the exchange of alkali ions of the glass with protons from the solution and also favour dissolution of germanium. From the result of Fig. 5, it may be found that pH increases with increasing leaching time. The variation of pH value in the 23–34 h stage is greater than that of other stages. It may be suggested that leaching for 34 h involves the formation of an alkali-deficient surface layer on the glass as a result of the more rapid extraction of alkali. Subsequent extraction of alkali involves diffusion of alkali through the layer from the glass towards the solution. Hydrogen ions from the solution diffuse in the opposite direction to maintain charge balance.[18]

The chemical resistance of C_1 and C_5 glasses is lower than that of other glasses, since mixed alkali glasses typically have higher chemical durabilities than single alkali glasses.[19] The alkali ion mobility in oxide glasses decreases drastically when a second alkali ion is introduced. This reduction in ion mobility rate is attributed to an increase in the activation energy.[10] In glasses where the alkali ion mobility controls the exchange rate for protons, the lower alkali ion mobility in mixed alkali glasses would be expected to lower the rate of chemical attack.

The mixed alkali effect on electrical resistivity of these germanate glasses is shown in Fig. 6. The maximum in electrical resistivity occurs at $Na_2O/(Li_2O + Na_2O) = 0.5$. The dependence of the magnitude of the maximum in resistivity upon the second alkali can also be accounted for by the

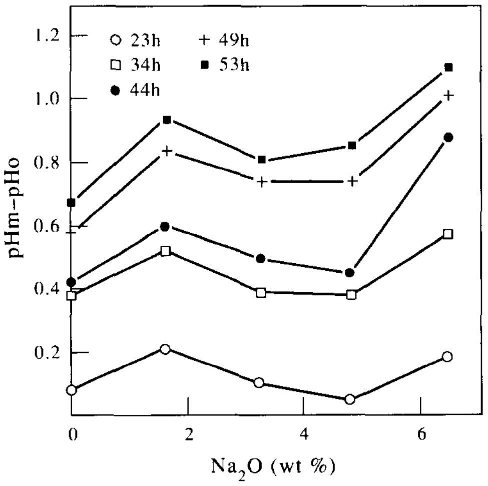

Fig. 5. Mixed alkali effect on pH change of calcium aluminogermanate glass in nitric acid solution at initial pH = 2.02 and 30 °C for various leaching time. pH_m = the pH value of the solution with sample after leaching test. pH_o = the pH value of the initial solution.

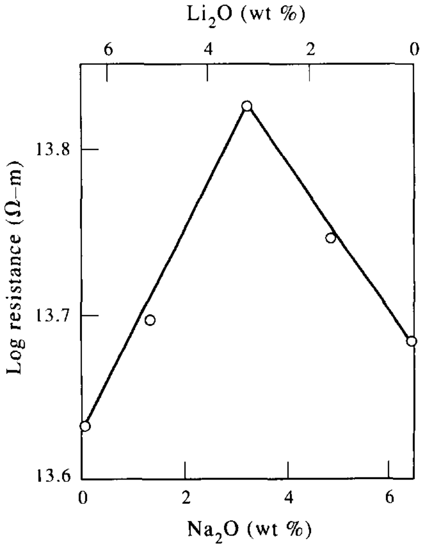

Fig. 6. Mixed alkali effect on the electrical resistivity of calcium aluminogermanate glasses.

compositional dependence of the alkali diffusion coefficients.[8] Varshneya[20] calculated that conductivity and diffusion coefficients from the modified Nernst–Einstein equation were:

$$\sigma = \frac{Ne^2}{kT}\left[\frac{(C_A - C_{AB})D_A}{f_A} + \frac{(C_B - C_{AB})D_B}{f_B}\right]$$

where σ is the electrical conductivity, N is the total number of alkali ions per unit volume, C_A is alkali ions, C_{AB} is the concentration of alkali ions not participating in the conduction process, D_A and D_B are diffusion coefficients of A and B ions, f_A and f_B are correlation factors in pure A and B end member glasses.

In the course of alkali transport in mixed alkali glasses, it is expected that smaller alkali ions enter sites vacated by larger alkali ions and larger alkali ions enter sites vacated by smaller alkali ions. Since the ionic motion is faster than the rate of structural relaxation,[21] these ions would be occupying 'wrong sites'.[10] Alkali ions in 'wrong sites' are constantly being created and annihilated by the motion of the alkali ions and the stress relaxation.[10] The lower conductivity of mixed alkali glasses is attributed to changes in both the distribution and size of these compositionally different regions, which are dependent on the total alkali content and different alkali ions present. The activation energy barrier for alkali ion mobility is influenced by the media surrounding the alkali.[8] In addition, it is assumed that the direct exchange of alkali ions does not take place in glasses; instead alkali ions are assumed to jump into vacancy or interstitial sites first.[8] The activation energy of electrical conductivity is expected to be high.

4 CONCLUSIONS

The results in this study are summarized as follows:

1. Germanate glasses containing 0–6.44 wt% Li_2O were prepared by progressive weight percent substitution of Na_2O for Li_2O, at a constant ratio of concentration of CaO, Al_2O_3 and GeO_2.
2. The results of FT-IR spectra show that the peak in these glasses corresponds to GeO_4 groups and the Ge remains in 4-coordination for these germanate glasses.
3. As $0 \leq Na_2O/(Li_2O + Na_2O) \leq 0.5$, the refractive index and reflectance decrease with increasing Na_2O content, while $1 \geq Na_2O/(Li_2O + Na_2O) \geq 0.5$, its values increasing with increasing Na_2O content.
4. pH value increased with increasing leaching time. The variation of pH in the 23–34 h stage is greater than that of other stages.
5. The maximum in electrical resistivity occurs at $Na_2O/(Li_2O + Na_2O) = 0.5$.

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